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Multifunctional hyperbranched polyester grafted β-cyclodextrin metal complexes for textile coating

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ABSTRACT

This study approached the developing of grafted beta cyclodextrins (β-CD) for achievement multifunctional properties. Hyperbranched bis-MPA-polyester-16-hydroxyl, generation 2, (HBPE-2) was used as crosslinker in the presence of cobalt (Co) or nickel (Ni) acetate using emulsion technique. The resulting materials were applied in the printing paste for *in situ* printing of cellulosic fabrics using phthalocyanine organic pigment (C.I: pigment blue 15:3). Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and particle size distribution analysis using dynamic light scattering (DLS) technique were examined to illustrate the structure and morphologies of the prepared materials. Moreover, the antimicrobial activity against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria using the agar diffusion method was also carried out. The FTIR results demonstrated that HBPE-2 can serve as a good crosslinker to obtain the grafted β-CD with high thermal stability and physical attachment relative to the uncrosslinked one. Also, TEM and particle size analysis indicated that successful metal binding to the grafted β-CD was obtained with different morphologies and low particle size relative the uncrosslinked one. All the grafted β-CD samples exhibited good antimicrobial activity up to 20 mg concentration. Besides, the prepared materials accelerated the colour fixation on the surface of the cellulosic fabric prints relative to the used conventional pigment printing under the unfavorable conditions.

Keywords: *Hyperbranched polyesters; beta cyclodextrin; metal complexes; antimicrobial activity; coating; fabric printing*

1. INTRODUCTION

Among all potential supramolecular hosts, cyclodextrins (CDs) appear to be the most significant ones, due to their seminatural items, which obtained from renewable common material, starch, by a generally basic enzymic transformation. Cyclodextrins are cyclic oligosaccharides having hydrophobic holes, which can tie substrates specifically and catalyze synthetic responses with high selectivity [1, 2].

In spite of the high productivity of response, simple partition and recuperation of beta-cyclodextrin (β-CD), notwithstanding, still stays a few issues. It cannot be utilized as an insoluble sorbent under some particular conditions, with the exception of after adjustments. For this reason, many research works are exposed to change crosslinking techniques for β-CD. The most widely recognized crosslinking operators incorporate epichlorohydrin, ethylene glycol diglycidyl ether and glutaraldehyde [4-5]. It can likewise be utilized in ecological assurance, since it effective immobilizing poisonous materials inside its depression. Besides, the coordination of β-CD with metal salts resulted in differences in thermal decomposition processes of β-CD/metal complexes [6, 7].

In recent years, hyperbranched polymers represented *via* dendrimers have received attention due to their multifunctional residences [8-11]. They do have certain hazards, however, such as low hiding strength, poor dispersion capability, and specifically negative weather durability. In addition, the absence of their fiber affinity needs the use of resinous binder to restore pigment particles on the fiber floor to accumulate color rapidity [12, 13]. Phthalocyanin pigment encapsulation on hyperbranched polyesters (HBPE) has been previously reported by our team for *in situ* cellulosic fabric printing [14].

The encapsulation was established by approached liquid-phase separation. In addition, the encapsulated colors (pigments or shades) increased the pigment print fixation in one step at once and reduced the necessary binder quantity and fixation temperature relative to the manipulated template. [15-26]. Moreover, the aggregate between hyperbranched polyesters (HBPE) and CD that having one-of-a-kind molecule cavities in their molecular architectures led to the enhancement of their molecular inclusion skills for small molecular visitors [27]. Moreover, the formerly synthesized β-CD based HBPE by means of a simple condensation method confirmed proper antimicrobial activity towards gram - positive (*B. subtilis*) and gram-negative (*S. aureus*) as nicely as fungi (*A. niger* and *C. albicans*) [28].

Recently, the usage of HBPE with chitosan resulted in novel multifunctional composite, due to its bodily and chemical special residences [29]. Besides, it has been used as the essential cloth for miscellaneous coating resins which includes powder coatings [30].

Herein, the purpose of this work was once to increase multifunctional grafted β-CD using hyperbranched bis-MPA polyester-16-hydroxyl, generation 2 (HBPE-2) in the presence of acetate salts of cobalt and nickel one at a time using emulsion technique. In this approach, the prepared materials have been used as binders in the printing paste for cellulosic fabric printing using C.I. pigment blue 15:3 through a flat silk screen method. The evaluation of the prepared materials was carried out using TEM morphological observation, Fourier transform infrared spectroscopy (FT-IR) and particle size distribution analysis using DLS technique. The influence of the variety of purposeful hydroxyl groups give up agencies on the printing manner of the printed

cellulosic fabrics used to be determined. The fundamental other objective was once to locate whether the HBPE-2 coating of pigment is more superb in saving time, energy and auxiliaries under the destructive conditions of printing manner than in our previous find out [31].

Furthermore, the antimicrobial activity of the prepared materials was examined against gram-positive *Escherichi coli* (*E. coli*) and gram-negative *Staphylococcus aureus* (*S. aureus*) bacteria using of agar diffusion method.

2. MATERIALS AND METHODS

2.1. Materials.

Misr El Mahalla Co., Egypt, supplied cotton and viscose fabrics (100 %) of 153 and 146 g / m2, respectively. The sample size used for printing had been 5. 10.10 cm. Previously they were scoured by soaping with (2 g / L) nonionic detergent solution (Clariant, Egypt's Hocstapal CV) at a liquor ratio of 1:25, at 60°C for 45 min, accompanied by washing and air-drying.PB 15:3 was provided by Dye Star, Egypt. Hyperbranched bis-MPA polyester-16-hydroxyl, generation 2 (HBPE-2) and β-CD were supplied by Sigma, Germany (Figure. 1).

Synthetic thickener Alcoprint (PTP) includes an acrylic copolymer and petroleum distillate (Solvent neutral 150) obtained with Clarient and Imperon Binder MTB acrylate-based copolymer dispersion (density 1.03 g / cm3 and viscosity 35–70 M Pas),were obtained from Hoechst, Germany. All pathogens were isolated and produced by Chemistry of Natural and Microbial Products Department, National Research Center, Egypt. All chemicals and other reagents were used as received, without further purification.

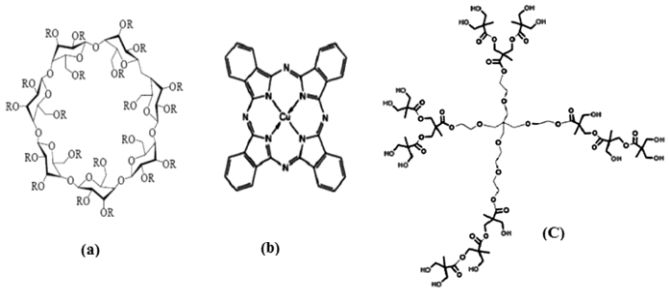

Figure 1. Chemical structures of (a) β-CD, (b) pigment blue and (c) HBPE-2.

2.2. Methods.

2.2.1. Preparation of the grafted β-CD with HBPE-2.

A definite amount (1 wt%) of β-CD was dissolved in hot aqueous medium containing 100 mg of potassium persulfate and 1 mL of polyvinyl chloride to obtain the solution (A).

Table 1. Chemical composition of the prepared materials**.**

Sample code	Chemical Composition			
	β-CD	HBPE-2	Co	Ni
(1)	1	0	0.5	0
(2)	1	0	0	0.5
(3)	1	0.5	0.5	0
(4)	1	0.5	0	0.5

Cobalt or Nickel acetate (0.5 wt%) was ultrasonically suspended in a solvent mixture of water/cyclohexane (1:1) containing 5 mg of palmitic acid and 2 mg of cetyl trimethyl ammonium bromide (CTBA) to obtain the solution (B). Solution B was slowly added to the solution (A) followed by addition of HBPE-2 (0.5 wt %) under stirring. The resulting mixture was ultrasonically treated for 30 min. The mixture was lift overnight, then the resulting material was collected, dried and kept for further investigation (Table 1).

2.2.2. Pigment printing of cellulosic fabrics.

For traditional and modified pigment printing of cellulosic fabrics, the paste formulation was prepared using the following recipe: pigment paint, 25 g / kg; synthetic thickener, PTP, 25 g / kg; binder (MTB) 100 g / kg, and water 850 g / kg. Although, in the case of modified printing: in the absence or presence of 25 g / kg binder, 50 g / kg of grafted beta cyclodextrins (Gβ-CD) was used. The impression pastes were applied via a flat silk screen to the fabrics. After printing, in an automated thermostatic oven, developed by Warner Mathis, Switzerland, the printed cellulosic fabrics using Gβ-CD were immediately subjected for curing without drying at 120 ° C for 3 min. The traditional ones were washed, then set for 5 min at 150 ° C. The printed samples were then washed at 60 ° C for 15 min with aqueous solution that contained (2 g / L) nonionic detergent.

2.2.2.1. Color strength.

A recording filter spectrophotometer was used to perform spectral reflex measurements of the dyed fabrics. The color intensity of the printed samples expressed as K/S values was calculated by applying the Kubleka – Munk equation for the pigment blue color at wave length max 580 nm and the pigment green at 625 nm:

$$K/S = (1-R)^2/2R-(1-R_0)^2/2R_0$$

Where R is the decimal fraction of the reflectance of the dyed substrate, R_0 is the decimal fraction of the reflectance of the unprinted substrate, S is the scattering coefficient and K is the absorption coefficient [32].

2.2.2.2. Fastness properties.

Washing rapidity tests were performed using the stated process, BS1006:C02 Test 2[33] with a soap solution (5 g / L, 50:1 liquor ratio) for 45 min at 48-50 ° C. The light-speed test was conducted using carbon-arc lamp based on the conventional methods for assessing textile color fastness.

2.2.3. In vitro antimicrobial activity.

The prepared materials were examined using agar diffusion method according to Cosentino *et al.*[34] and Haroun *et al.*[35-37].

2.2.3.1. Antimicrobial culture preparation.

Nutrient media was prepared according to manufactures instructions (10 g/L glucose, 6 g/L peptone, 3 g/L yeast, 1.5 g/L meat extract and 28 g/L agar) sterilized for 20 min at 120 ◦C. The following pathogens were used for this test:

• Gram positive (+) bacterium such as: *Staphylococcus aureus* (S. aureus).

• Gram negative (−) bacterium such as: *Escherichia coli (E. coli).*

Inhibition zone technique

All above bacteria were cultured overnight at 37ºC for 24 h in the nutrient media, while the yeast was cultured at 27ºC for 48 h in potato dextrose agar media (PDA). Each culture media was

diluted with sterile 0.9% saline solution (1:1000) to give a suspension of about 5×10^9 microorganisms per mL.

2.2.3.2. Minimum inhibition concentration (MIC).

Different concentrations of the prepared materials (2, 5, 10, 15 and 20) mg were suspended in THF solvent and then used to saturate 6 mm filter paper discs. The discs were placed on PDA and nutrient agar media that were previously inoculated with the tested microorganisms. The Petri dishes were incubated at 37ºC for tested bacteria. MIC was defined as the lowest concentration that inhibits the visible growth of the microorganism after the incubation period. All the experiments were done in triplicate to confirm the data.

2.3. Characterization.

Fourier transform infrared spectra (FTIR) of the prepared materials in the range 500-4000 cm^{-1} using potassium bromide pellet, were recorded on Nicolet Impact-400 FTIR spectrophotometer. Morphologies of the prepared materials were characterized by JEOL-transmission electron microscope (TEM). After centrifugation and dispersion in distilled water, the samples were examined and lowered onto a plate, drying at room temperature. Then, they were vacuum-coated with a gold and palladium mixture for 3 min. The size distribution was calculated by a laser diffraction method operated by Zetasizer Nano-ZS (Malvern Instruments, UK). The particles were defined by the mean diamete intensity. Samples were diluted 2000 times and ultrasonicated before recording.

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared materials.

The prepared grafted β-CD using HBPE-2 had countless advantageous as an alternative than that formerly reported *via* Zhao *et al.*[38] that the use of epichlorohydrin as crosslinker for practice of novel gels based totally on crosslinked β-CD.

The adsorption capability of these substances is regularly decreased as the answer temperature and pH rise. Figure 2 shows FTIR spectra of original β-CD in comparison with the prepared materials (1) β-CD/Co, (2) β-CD/Ni, (3) β-CD/HBPE-2/Co and (4) β-CD/HBPE-2/Ni. It was found that both β-CD and HBPE-2 contained large OH groups which appeared as a broad peak around 3422 cm^{-1}. This is additionally attributed to the presence of a widespread quantity of the bounded water. Besides, this broad complex OH stretching band is due to the combined effect of the differently associated hydroxyl groups such as intra/intermolecular hydrogen bonding between different –OH groups (in case of the original β-CD) or between the free –OH and –C=O in case of the grated β-CD [39]. On the other hand, the peak at 1731 cm^{-1} is assigned to the –C=O group of the ester linkages.

The decreasing and shifting of the carbonyl group in case of the grafted samples may be attributed to the formation of the chelating complex between the Co or Ni atoms and –C=O of HBPE-2 which weakens the double bonding property of carbonyl groups owing coordinate bond between oxygen atoms and metal ions [40]. The presence of the ester groups is also confirmed by the appearance of the peaks at 1000-1320 cm^{-1} corresponding to the –C-O and C-O-C stretching vibrations due to the linkage between the metal ions and the terminated hydroxyl groups.

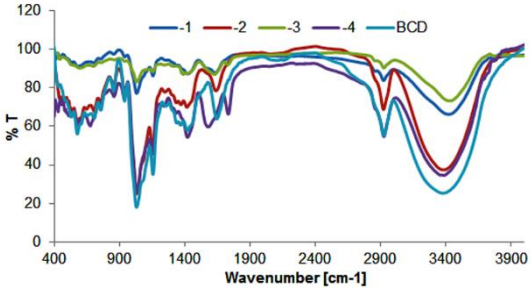

Figure 2. FTIR spectra of the prepared materials (1) β-CD/Co, (2) β-CD/Ni, (3) β-CD/HBPE-2/Co and (4) β-CD/HBPE-in comparison with the relative to the free one.

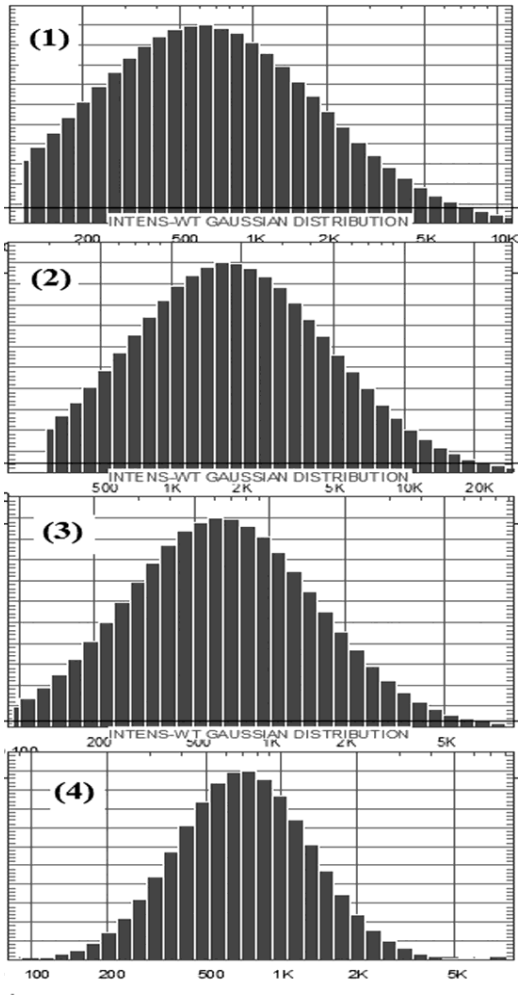

Figure 3. Particle size distribution analysis of the prepared materials (1) β-CD/Co, (2) β-CD/Ni, (3) β-CD/HBPE-2/Co and (4) β-CD/HBPE using DLS technique.

Figure 3 and Table 2 show the particle size distribution analysis of the prepared materials using DLS technique. It can be seen that the grafted β-CD with HBPE-2 exhibited low particle size in the presence of Co or Ni metal ions (938 and 858 nm, respectively) in comparison with hat in the case of the β-CD metal complexes (1135 and 2932 nm, respectively). In addition, the presence of HBPE-2 caused a significant decreased in polydispersity indexes (PDI), which turn increased the dispersion of the grafted β-CD metal complexes. This may be due to the terminal hydroxyl groups (-OH) were binding with the metal ions (Co or Ni) and decreased the repulsive charges on the grafted β-CD. In other words, the free negative surface charges of –OH groups

were consumed on the grafted β-CD with HBPE-2. This confirmed by the significant decrease in the PDI.

Table 2. Particle size distribution analysis of the prepared materials using DLS technique.

Sample code	Particle size (nm)	PDI
(1)	1135±1.11	1.24
(2)	2932±1.01	1.03
(3)	938±0.88	0.785
(4)	858±0.63	0.397

TEM images were obtained as shown in Figure 4. It is clear that the prepared grafted β-CD had big structure areas more likely coming from the aggregation of individual β-CD molecules. Besides, dark Co cores were surrounded by grey β-CD shells suggesting the successful coating process. It is known that β-CD can form host-guest complex which depends on the size, shape and hydrophobicity of the guest molecule as reported previously by Zhu *et al.* [41].

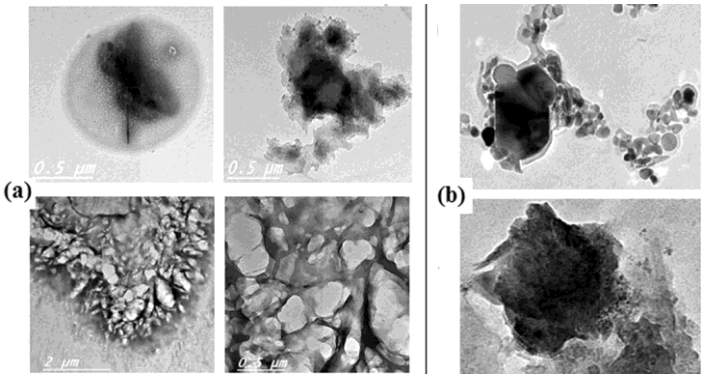

Figure 4. TEM images of the prepared materials (a) samples (1) and (2) at 500 nm resolution and (b) samples (3) and (4) at 200 nm resolution.

3.2. Pigment printing.

Modification of organic pigments drawn closer by means of many researchers is the predominant riding pressure to quicken the pigment printing processing and enhance its dispersions stability, for that reason prevents the flocculation and the coagulation of the pigments [42]. In our previous work [43], we reported the encapsulation of phthalocyanine pigment blue onto citric-acrylate oligomer and hyperbranched polyesters using different generations for enhancement of pigment printing process. The cellulosic fabrics can be printed at a curing temperature 120°C without drying in one step and with a reduced amount of binder, 50 g/kg and 35 g/kg, respectively and eliminating the use of acid catalyst. However, the un-encapsulated pigments seemed to require a conventional condition of duration, temperature and auxiliaries in order to get reasonable colour strength, and could not be processed under the unfavorable conditions. In other words, the modified pigment printing process exhibited several advantages for printing technology of cellulosic fabrics. Hence, it would be interesting to investigate multifunctional modification of pigment with other effective materials that can provide a powerful tool for acceleration of pigment printing process on the cellulosic fabrics. The grafted beta cyclodextrin (Gβ-CD) would be as an alternative for binder in the printing formulation. The high solid content relied the presence of binder could restrict their use in textile fields as they are unable to meet the wearability and comfort requirements for textiles with respect to fine patterns and soft fabric handle. This could be eliminated the surface roughness effect of binder and increased the durability properties, rubbing, washing, and light of printed fabrics. It is clear from Table 3 that the proposed aim for preparation of Gβ-CD could be achieved for eliminating binder and got reasonable colour strength and durability properties on cellulosic fabrics at low concentration in absence of binder compared to the conventional ones. It is also clear that the printed cellulosic fabrics using the Gβ-CD in absence of binder displayed higher colour strength than the conventional printed samples. In other words, the combination between hyperbranched polyesters (HBPE) and β-CD in the presence of the metal are influential and could have a rapid printing balance and reasonable color strength on cotton and viscose fabrics at low fixation temperature without drying in absence of binder. This could be attributed to the structure feature of the Gβ-CD which bear a more terminated hydroxyl groups and binding core metals that could interact with cellulosic fabrics through a chelating or physical interaction modes. These various modes of interactions through the prepared materials minimized the driving forces of pigment printing and eliminated the use of resinous binder. It is clearly seen that the approached trial for presence of 25% of binder with the prepared materials has no noticeable effect on the color strength of printed cellulosic fabrics. The other point of interest was to determine the durability properties of printed cellulosic fabrics using the Gβ-CD in absence of binder throughout washing, crocking and light. In other words, the results of this study in Table 3 indicated that the fastness properties of the majority of printed cotton and viscose sample using Gβ-CD were higher than that of using the conventional ones.

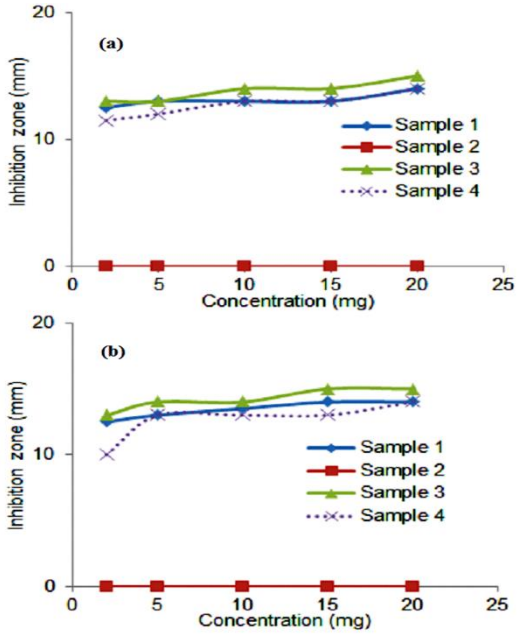

Figure 5. *In vitro* antimicrobial activity of the prepared materials at different concentrations against (a) *S. aureus* and (b) *E. coli* using agar diffusion method.

This better fixed printability as a consequence of Gβ-CD interaction with cellulosic fabrics by various modes of interactions. It is demonstrated that the Gβ-CD increases the resistance of printed fabrics against the photo fading as was arisen from the excellent rating of light fastness. Moreover, the use of Gβ-CD and elimination of binder was influential and increases the crocking fastness properties of printed fabrics compared to conventional ones.

3.3. *In vitro* antimicrobial activity.

The encapsulation of pigment by Gß-CD exhibited for the prepared powder forms certain antibacterial efficiency against *E. coli* and *S. aureus* bacteria. The antibacterial activity was evaluated by measuring the clear zone inhibition around the test sample after 24 h incubation as described in the experimental section. Tetracyclin antibiotic was used as a reference in this test. Figure 5 shows the effect of the Gß-CD-encapsulation of pigment on the antibacterial properties. As expected, no inhibition zones were observed for the un-encapsulated pigment powder indicating that the conventionally pigment colour has no antibacterial properties against *E. coli* and *S. aureus* bacteria. On the other hand, the results reported that the encapsulated pigment showed good antibacterial activities against the aforementioned organisms compared with Tetracyclin antibiotic reference. This may be due to the presence of the different anionic groups in the shell. The differences observed in the diameter of the zone of inhibition between the different formulations may be due to the difference in the susceptibility of bacteria to the samples. It was obviously clear that the tested samples are effective in controlling *S. aureus* growth higher than *E. coli.* This may be attributed to the thick layer around the cell wall of *E. coli* which resists the penetration of antibacterial active material to their cell walls to interfere in its metabolic pathway.

Table 3. The fastness properties of the printed cellulosic fabrics using the prepared metal complexes as binders *via* silk screen printing method in comparison with the conventional technique.

Sample Code	/Cellulosic Fabrics		Washing Fastness			Light Fastness	Rubbing Fastness		K/S	Handle
			Alt	Stc	Stw		Wet	Dry		
(3)	C	binder*	4-5	4	4	6	3-4	3-4	13.7	S
		without	4	4	4	7	3-4	4	12.1	S
	V	binder	4-5	4	4	6	3	3-4	13.9	S
		without	4	4	4	7	3-4	4	12.5	S
(4)	C	binder	4-5	4	4	6	3	3	12.2	S
		without	4	4	3	7	4	4	10.8	S
	V	binder	4-5	4	4	6	3	3-4	13	S
		without	4-5	3-4	3	7	4	4	11.3	S

Conv.: Conventional technique, C: Cotton fabric, V: Viscose fabric, Alt: Alteration, Stc: Staining on cotton fabric, Stw: Staining on woolen fabric, H: harsh feeling, S: soft feeling, *binder concentration 2.5%.

4. CONCLUSIONS

The successful grafting of β-CD using HBPE-2 in the presence of Co or Ni metal salt was confirmed by FTIR, TGA and TEM results. The combination of both β-CD and HBPE-2 demonstrated that their inclusion capabilities for small molecular guests were enhanced due to their different topographical architectures.

The enhanced microbial behavior of the grafted ß-CD with HBPE was due to the hydrophobic nature of the polymer and a large number of alkyl chains attached to it. On the other hand, the Gβ-CD could be used as an alternative for binder at low concentration. The novelty of this work has arisen from its ability to fit the requirements of the wearability and comfort for pigment prints in textile fields with term to fine patterns and soft fabric handle and develop antimicrobial properties on cellulosic fabrics.

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6. ACKNOWLEDGEMENTS

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